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## Dinuclear palladium(I) sandwich complexes of furan and toluene



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### ABSTRACT

The reaction of a dinuclear palladium complex  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{X}]_2$  ( $\text{X} = \text{BF}_4, \text{PF}_6$ ) with excess furan afforded the sandwich-type bis-furan dinuclear palladium(I) complex  $[\text{Pd}_2(\mu\text{-furan})_2(\text{CH}_3\text{CN})_2][\text{X}]_2$ . The substitutionally labile bridging furan ligands in the dipalladium sandwich complex can be readily replaced with toluene to give the bis-toluene dipalladium(I) sandwich complex  $[\text{Pd}_2(\mu\text{-toluene})_2(\text{CH}_3\text{CN})_2][\text{X}]_2$ .

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## 1. Introduction

Increasing attention has been paid to the organopalladium complexes containing a Pd–Pd bond [1]. The coordination behavior or transformation of unsaturated hydrocarbons at a dinuclear palladium center has been investigated by employing reactive  $\text{Pd}^{\text{I}}\text{–Pd}^{\text{I}}$  complexes [1]. Representatively, the homoleptic nitrile dipalladium(I) complexes  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{X}]_2$  (**1**,  $\text{X} = \text{BF}_4$ ; **1'**,  $\text{X} = \text{PF}_6$ ) have been developed as the substitutionally labile Pd–Pd complexes for studying coordination modes and reaction patterns of unsaturated substrates at a dinuclear palladium center [2,3]. By employing **1**, indeed, several new coordination modes or reaction patterns have been

recently disclosed in our laboratory, such as dinuclear palladation of arenes [4] and the bridging  $\pi$ -coordination of pyrrole and indole [5]. Agapie et al. reported the bridging  $\pi$ -coordination of thiophene and furan to a diphosphine-arene supported  $\text{Pd}^{\text{I}}\text{–Pd}^{\text{I}}$  moiety [6]. Here, we report the sandwich-type bridging  $\pi$ -coordination of furan and toluene to a dicationic  $\text{Pd}^{\text{I}}\text{–Pd}^{\text{I}}$  moiety.

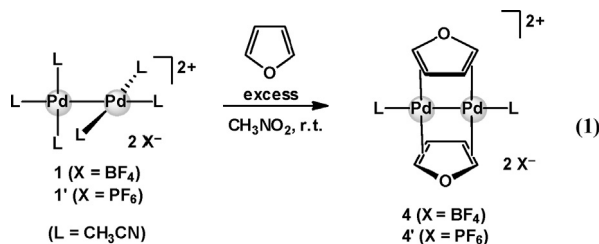
## 2. Results and discussion

The coordination behavior of weakly coordinating organic substrates such as arenes and hetero-arenes to a  $\text{Pd}^{\text{I}}\text{–Pd}^{\text{I}}$  moiety may be addressable when highly substitutionally labile  $\text{Pd}^{\text{I}}\text{–Pd}^{\text{I}}$  complexes are used as the starting materials. We recently reported the bridging  $\pi$ -coordination of pyrrole or indole to a dicationic  $\text{Pd}^{\text{I}}\text{–Pd}^{\text{I}}$  moiety derived from  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$  (**1**) [5]. The resultant  $\mu$ -pyrrole  $\text{Pd}_2$  complex  $[\text{Pd}_2(\mu\text{-pyrrole})_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$  (**2**) or  $\mu$ -indole  $\text{Pd}_2$  complex  $[\text{Pd}_2(\mu\text{-indole})_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$

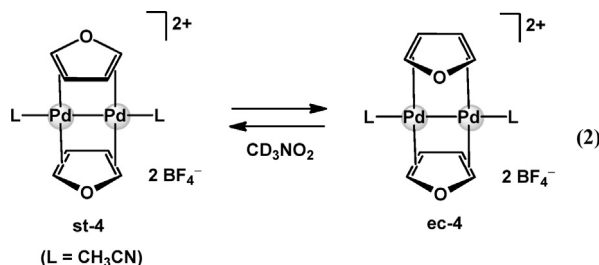
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(3) are stable in solution at ambient temperature, while the  $\pi$ -adducts of non-chelating, parent pyrrole or indole to mononuclear  $\text{Pd}^{\text{II}}$  or  $\text{Pd}^0$  moieties have not been isolated so far. As a part of our study on the bridging  $\pi$ -coordination of weakly coordinating arenes and hetero-arenes [4,5], here, we employed furan as the bridging substrate. Addition of furan (2 equiv) to **1** in  $\text{CD}_3\text{NO}_2$  at ambient temperature showed no sign of furan coordination in the  $^1\text{H}$  NMR spectra. However, precipitation from the solution of **1** or **1'** in  $\text{CH}_3\text{NO}_2$  in the presence of a large excess of furan gave the bis-furan sandwich complex  $[\text{Pd}_2(\mu\text{-furan})_2(\text{CH}_3\text{CN})_2][\text{X}]_2$  (**4**,  $\text{X} = \text{BF}_4$ ; **4'**,  $\text{X} = \text{PF}_6$ ) (Eq. 1). A single crystal of **4** suitable for X-ray structure analysis was obtained through vapor diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_3\text{NO}_2$  solution at ambient temperature. The molecular structure of **4** was shown in Fig. 1. The furan ligands coordinate to a  $\text{Pd}^{\text{I}}\text{-Pd}^{\text{I}}$  moiety via  $\mu\text{-}\eta^2\text{:}\eta^2$  bridging mode in a mutually staggered arrangement (**st-4**). The  $\text{Pd}\text{-Pd}$  bond length (2.486(2) Å) is in the range of normal  $\text{Pd}^{\text{I}}\text{-Pd}^{\text{I}}$  lengths [1a], and is similar to that of the bis-pyrrole  $\text{Pd}_2$  complex **2** ( $\text{Pd}\text{-Pd} = 2.4783(9)$  Å) [5]. A longer  $\text{Pd}\text{-Pd}$  bond was reported in a 2-methylfuran-bridged  $\text{Pd}_2$  complex  $[\text{Pd}_2(\mu\text{-2-methylfuran})(\mu\text{-terphenyl-diphosphine})][\text{BF}_4]_2$  ( $\text{Pd}\text{-Pd} = 2.6518(9)$  Å), where the back-side bridging ligand is the  $\mu\text{-}\eta^2\text{:}\eta^2$ -arene ring [6].



The  $^1\text{H}$  NMR spectra of **4** in a mixed solvent  $\text{CD}_2\text{Cl}_2\text{-CD}_3\text{NO}_2$  at  $25^\circ\text{C}$  exhibited two broad resonances for the furan protons at  $\delta_{\text{H}2} = 8.57$  ppm (2-position) and  $\delta_{\text{H}3} = 6.98$  ppm (3-position). Lowering the temperature down to  $-50^\circ\text{C}$  caused each resonance to decoalesce to two resonances, indicating a rapid equilibrium between two isomers (major/minor = 62/38; for major isomer,  $\delta_{\text{H}2} = 8.63$  ppm and  $\delta_{\text{H}3} = 6.88$  ppm; for minor isomer,  $\delta_{\text{H}2} = 8.19$  ppm and  $\delta_{\text{H}3} = 6.95$  ppm). There are two possible isomers for the  $\mu\text{-}\eta^2\text{:}\eta^2$ -furan sandwich, i.e. a staggered arrangement (**st-4**) and an eclipsed arrangement (**ec-4**), where the former was identified in the crystalline state. In solution, presumably, these two possible isomers **st-4** and **ec-4** exist in equilibrium (Eq. 2). The bis-furan dipalladium complex **4** gradually decomposed in  $\text{CD}_3\text{NO}_2$  at ambient temperature.



We confirmed that the bridging furan ligands in **4** or **4'** are easily replaced with toluene or pyrrole. Addition of large

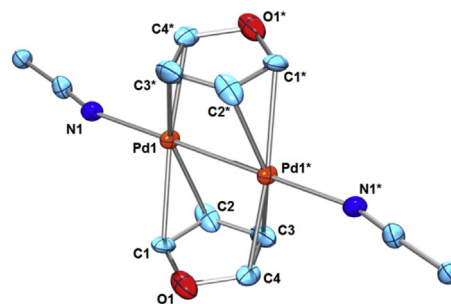
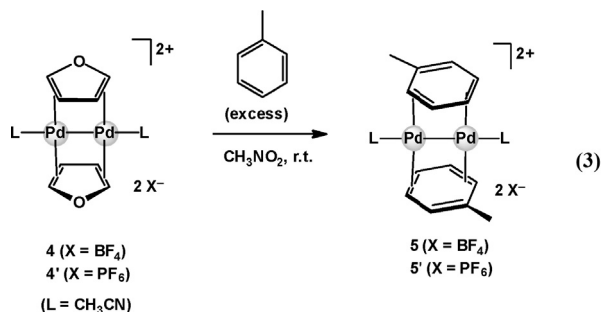


Fig. 1. (Color online.) ORTEP of  $[\text{Pd}_2(\mu\text{-furan})_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$  (**4**) (30% probability ellipsoids; hydrogen atoms and counter anions are omitted for clarity. Selected bond lengths (Å):  $\text{Pd1-Pd1}^* 2.486(2)$ ,  $\text{Pd1-C1} 2.28(3)$ ,  $\text{Pd1-C2} 2.27(2)$ ,  $\text{Pd1-C3}^* 2.31(2)$ ,  $\text{Pd1-C4}^* 2.25(2)$ ,  $\text{Pd1-N1} 2.13(2)$ ,  $\text{C1-C2} 1.30(4)$ ,  $\text{C2-C3} 1.42(3)$ ,  $\text{C3-C4} 1.31(4)$ ,  $\text{C4-O1} 1.39(3)$ ,  $\text{O1-C1} 1.36(2)$ .

excess toluene to a  $\text{CH}_3\text{NO}_2$  solution of **4** or **4'** afforded the bis-toluene dipalladium(I) complex  $[\text{Pd}_2(\mu\text{-toluene})_2(\text{CH}_3\text{CN})_2][\text{X}]_2$  (**5**,  $\text{X} = \text{BF}_4$ ; **5'**,  $\text{X} = \text{PF}_6$ ) (Eq. 3). A related dicationic bis-benzene dipalladium complex  $[\text{Pd}_2(\mu\text{-benzene})_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$  was recently prepared directly from **1** in the presence of a large excess of benzene [4], but its structure has not been determined by X-ray structural analysis. A single crystal of **5** or **5'** suitable for X-ray analysis was obtained by recrystallization from  $\text{CH}_3\text{NO}_2$ /toluene at  $-30^\circ\text{C}$ . The molecular structure of **5'** is shown in Fig. 2. The two toluene ligands coordinate to a  $\text{Pd}\text{-Pd}$  moiety ( $\text{Pd}\text{-Pd} = 2.5651(4)$  Å) in a  $\mu\text{-}\eta^2(\text{C1-C2})\text{:}\eta^2(\text{C3-C4})$  manner (Fig. 2). The related neutral bis-toluene  $\text{Pd}_2$  sandwich complexes,  $\text{Pd}_2(\mu\text{-toluene})_2(\text{GaCl}_4)_2$  (**6**),  $\text{Pd}_2(\mu\text{-toluene})_2(\text{GaBr}_4)_2$  (**7**), and  $\text{Pd}_2(\mu\text{-toluene})_2(\text{Ga}_2\text{Cl}_7)_2$  (**8**), were structurally characterized by Kloo et al.; in each case, the coordination mode of toluene is in a  $\mu\text{-}\eta^2(\text{C1-C2})\text{:}\eta^2(\text{C3-C4})$  mode or a  $\mu\text{-}\eta^2(\text{C1-C2})\text{:}\eta^2(\text{C4-C5})$  mode [7–9]. Concerning the arene rings, uncoordinated  $\text{C5-C6}$  (1.379(5) Å) is considerably shorter than other C–C ring bonds ( $\text{C1-C2}$ ,  $\text{C2-C3}$ ,  $\text{C3-C4}$ ,  $\text{C4-C5}$ , and  $\text{C1-C6}$  are in the range of 1.406(5) Å–1.429(7) Å).  $^{13}\text{C}$  NMR spectra of **5** in  $\text{CD}_3\text{NO}_2$  showed the averaged resonance for the ortho- or meta-carbons at  $25^\circ\text{C}$  ( $\delta = 112$  ppm for ortho-carbons,  $\delta = 106$  ppm for meta-carbons). The  $^{13}\text{C}$  NMR resonance pattern for the toluene ligands did not change, even at lower temperature down to  $-20^\circ\text{C}$  in a mixed solvent  $\text{CD}_3\text{NO}_2\text{-CD}_2\text{Cl}_2$ , indicating the rapid fluxional behavior of the  $\mu\text{-toluene}$  ligands in solution. The bis-toluene dipalladium complex **5** decomposed gradually in  $\text{CD}_3\text{NO}_2$  solution at ambient temperature.



Treatment of the bis-furan dipalladium complex **4** with pyrrole (2 equiv) in  $\text{CD}_3\text{NO}_2$  at ambient temperature

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